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## THE RELATION OF THE NITRATES TO THE PUTRESCIBILITY OF SEWAGES.\*

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Weldert has rather recently called attention to the treatment of sewages and sludges by the addition of nitrates in the form of saltpeter, and several workers as Guth and Keim,<sup>2</sup> Bach,<sup>3</sup> and Glaser<sup>4</sup> have since done considerable practical and research work on the same question. The subject is by no means a new one. As far back as 1892 Parry and Adeney<sup>5</sup> in an article entitled "Purification of Sewage by Microbes" recommended the addition of nitrates to sewage to prevent its becoming putrescent. The practical experiments of the two last named authors extended over four years. The sewage was first strained and treated with manganate of soda before the saltpeter was added. The addition of saltpeter to supply the sewage with the oxygen necessary to make it stable was not offered at that time as a final solution of the problem, but was regarded as very promising in its possibilities. At the time when the article appeared, knowledge of the importance of bacteria and enzymes in the biologic treatment of sewage was already well established. Even previous to these experiments it was known that nitrates would disappear quickly from sewage on standing, particularly when the temperature was favorable.

Scott-Moncrieff<sup>6</sup> had a process patented in 1898, which consisted in the addition of a highly nitrified filter effluent to septic tank sewages in order to make the sewage more suited for further biologic treatment. Fowler<sup>7</sup> experimented in 1900 on the purification of septic tank sewage by the addition of filter effluents. All of these experiments seemed to have given results which the excellent have

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<sup>&</sup>lt;sup>1</sup> Mitt. kgl. Prüfungsanst. Wasserversorgung, 1910, 13, p. 96.

<sup>&</sup>lt;sup>2</sup> Ges. Ing., 1912, 35, p. 57. <sup>5</sup> Eng. Record, 1892, 26, p. 380.

<sup>3</sup> Ibid., p. 341. 6 English Patent, No. 4994.

<sup>4</sup> Arch. f. Hyg., 1913, 80, p. 165. 7 The Manchester Sewage Works (Suppl.), 1900.

apparently been ignored until recently, when interest in the subject was again renewed.

Weldert speaks very enthusiastically of the possibilities of the application of saltpeter to sewages and sludges and urges sewage experts to try the process under various conditions. The consensus of opinion among recent observers has been that the process is too expensive to be of more than theoretical interest. Anyone interested in the complete bibliography of the process will find a list of references appended in Guth and Keim's, and Glaser's articles.

Weldert finds that the quantity of saltpeter required to make a sewage non-putrescible will vary with the concentration of the sewage and its state of decomposition. Sufficient time must be given for the completion of the reaction, which has been found to be between two and four days. The experiments were made with domestic sewages and sewages containing more or less trade waste. A medium temperature is most suitable. The quantity of Chile saltpeter required to make the sewage stable varied from 834 to 8,340 pounds per million gallons of settled sewage. Guth and Keim worked with stale hospital sewage, fresh domestic sewage, and creamery and brewery trade waste. As far as the trade wastes were concerned the result was unsatisfactory and biologic treatment seemed indispensable. Good results were obtained, however, with the other sewages on the addition of 4,170 to 8,340 pounds per million gallons of sewage, the quantity depending upon the concentration. Bach of the Emschergenossenschaft applied quantities of saltpeter, in some cases as high as 25,020 pounds per million gallons of sewage, permitting four days' contact, but on the whole he found 8,340 pounds sufficient. Glaser, the latest observer, found on experimenting with domestic sewage of Vienna that like quantities were required to obtain satisfactory results. When four grains of saltpeter were added to one gallon of sewage, methylene blue still retained its color after three days. A close agreement in the quantities of saltpeter necessary can be noted among those observers. The saltpeter employed in the practical tests was Chile saltpeter, which is crude sodium nitrate of approximately 90 per cent purity, while the laboratory tests were made with the crude and the pure salt.

All of the practical workers agree that the necessary period of contact with the sewage and the cost of the chemical make the treatment impracticable, as simple and successful as it is. Weldert figures the cost of the sewage treatment on the basis of his experiments as varying between \$18 and \$180 per million gallons, and the cost of the sludge treatment as varying between \$0.06 and \$0.32 per cubic yard. Two and one-half to 13.5 pounds of Chile saltpeter were added to one cubic yard of sludge to prevent the formation of hydrogen sulfid, which usually accompanies the decomposition of the sludge.

There is also a fairly close agreement on the physical and chemical changes brought about in sewages by the addition of saltpeter. It is claimed that sewage containing a sufficient amount of saltpeter never develops a putrid odor, that the clearness is increased, and that the organic nitrogen, free ammonia, and "oxygen consumed" are decreased, often, however, but very slightly. Guth and Keim showed that the alkalinity is increased at the end of the reaction due to the combination of the saltpeter sodium and the carbon dioxid.

Opinions on the mechanism of the reaction vary greatly. question is still an open one, altho it is certain that the presence of microorganisms is essential. Guth and Keim demonstrated that bacterial development is not retarded on the addition of saltpeter and that its action is not that of a preservative. No reduction took place on the addition of saltpeter to sterile sewage. Letts, Blake and Totton<sup>1</sup> give a description of the chemical products formed when saltpeter is added to sewage. The nitrate nitrogen was found in their experiments to be converted into free ammonia and nitric oxid; often only free nitrogen was formed. There is no evidence from those authors' experiments which would show that any considerable quantity of these gases was produced from either the free ammonia or the organic nitrogen present. "The process is one of combustion, the oxygen of the potassium nitrate appearing either partly or entirely in the form of carbon dioxid." In some of the experiments (anaerobic incubation of sewage with saltpeter) a little nitrite was produced, but ordinarily no nitrite could be

<sup>1</sup> Chem. News, 1903, 88, p. 182.

detected at the end of the reaction. The formation of free nitrogen on the addition of saltpeter to sewage has also been observed by others. Contrary to Bach and Guth and Keim, Glaser claims that the reduction to free nitrogen takes place directly and that no nitrite is formed during the process.

In the United States, a limited amount of work on the addition of saltpeter to sewage on contact filters was done at the experimental sewage testing station at Columbus, Ohio, during 1904-5. Sodium nitrate was added, in quantities of 20 to 30 parts per million of nitrogen as nitrates, to the contact filters to stimulate nitrification. The sewage was permitted to stand for eight hours. The application did not seem to have any influence upon the oxygen in solution, but a considerable decrease of "oxygen consumed" was noted. The reduction of the applied nitrate nitrogen within the first one or two hours was marked. In a number of subsequent experiments the period of contact with saltpeter was allowed to reach one week. No permanent improvement was noted. but it was observed with interest, that the last portion of the nitrate was reduced very slowly and that the organic nitrogen and "oxygen consumed" were decreased when the period of contact reached 24 to 48 hours. It was thought that the nitrate might supply the difference in oxygen, thus establishing more effective bacterial conditions. In this the experiments have been disappointing.

Some of my experiments given later are somewhat in line with the ones made at Columbus. Undoubtedly there must have been an improvement in the stability of the treated sewage in Columbus, which, however, is not indicated in the report. Unfortunately the addition of saltpeter cannot take the place of free oxygen in the immediate destruction of organic matter, but it will be noted later that it results in the shortening of the ultra-anaerobic period. The nitrate oxygen must be utilized by the bacteria and thus improve the sewage or effluent sooner or later. Anyone expecting immediate benefits from the saltpeter treatment is bound to be disappointed.

The attention of the writer was first drawn to this subject while investigating the rôle played by the nitrate oxygen and the free

G. A. Johnson, Report on Sewage Purification at Columbus, Ohio, p. 254.

dissolved oxygen in Spitta and Weldert's methylene blue putrescibility test. The results obtained in this investigation seemed of sufficient interest to be reported. Spitta and Weldert<sup>1</sup> were the first to utilize the decoloration of methylene blue in the absence of oxygen as an index of the degree of the putrescibility of a liquid. This test, which is almost universally used at present, has been investigated in this country in particular by Phelps and Winslow,<sup>2</sup> and the time of decoloration on anaerobic incubation has been found to coincide with the disappearance of the total available oxygen consisting of the free, nitrate, and nitrite oxygen. These forms of oxygen are given here in the order in which they were found to disappear. Abroad, the time required for decoloration serves as the expression of the degree of putrescibility of a sewage, effluent, or contaminated water, while in this country it is customary to report, as suggested by Phelps,3 the degree of putrescibility of a given sample in terms of "relative stability," which indicates the ratio of the available oxygen to the oxygen required for complete oxidation. It is pretty well established that the appearance of gases, such as hydrogen sulfid, which formerly served as the most reliable index of putrefactive conditions, coincides closely with the formation of the colorless leuko-base of the organic dve.

Since there is no doubt that putrefactive conditions will not set in as long as available oxygen is present in any form, it seemed of interest to look closer into the time element required for the utilization of the nitrate-nitrite oxygen versus the free oxygen by the bacterial flora. The question is one of importance, since the absence of the free oxygen is often looked upon as the sole index of undesirable conditions. The fact is, that at times there may be enough nitrate and nitrite oxygen present to prevent an actual nuisance and that there is a tendency to overlook this point.

My experiments were carried on at first without the artificial addition of mineral nitrogen. Crude domestic sewage, settled and septic sewage, and sprinkling filter effluents from the sewage testing station of the Sanitary District of Chicago were employed, and later the water from the main channel of the Sanitary District of Chicago.

<sup>&</sup>lt;sup>1</sup> Mitt. kgl. Prüfungsanst. Wasserversorgung, 1906, 6, p. 161.

<sup>2</sup> Jour. Infect. Dis., Suppl. 3, 1907, p. 1.

<sup>3</sup> Contrib. from Sanit. Research Lab. and Sewage Exper. Sta., 1909, 5, p. 77.

The Winkler method, as fully described in the "Standard Methods" of the American Public Health Association, has been employed for the determination of the dissolved oxygen in these experiments. In some of the later experiments, when nitrates were added, nitrites formed in some cases in sufficient amounts to make the endpoint in the titration a difficult one to observe. The method of Rideal and Burgess, which is the Winkler process modified into a colorimetric method, has given fairly satisfactory results in such cases. In short, the method consists in the comparison of the colors obtained in the routine of the Winkler method after the addition of the acid with standards prepared by adding varying definite quantities of potassium permanganate to bottles containing some potassium iodid in acid solution. Fairly accurate readings can be obtained after a little practice. Care must be taken to keep the standards in the dark when not in use and to renew them frequently. The nitrites are determined separately. One atom of oxygen is allowed for two atoms of nitrous nitrogen and the amount is subtracted from the total colorimetric reading obtained. An accurate titration method is undoubtedly to be preferred to a colorimetric procedure, but where close accuracy is not a sine qua non it is a convenient one. The method has been applied in only one set of the experiments, that is in the experiments in which saltpeter was added in open vessels to sewages and effluents in order to observe the reabsorption of oxygen by the liquids. Even then the samples were titrated except for the short periods of high nitrites during the "nitrate digestion" process, if I may be permitted to call it that. A more detailed study of the colorimetric Rideal-Burgess method is being carried on in the laboratory of the Sanitary District at present. The putrescibility tests were carried on for the most part in eight-ounce glass-stoppered bottles and the quantity of methylene blue calculated so as to give 1 c.c. of a 0.05 per cent watery methylene blue solution for each 150 c.c. bottle capacity, which is within the requirements of the "Standard Methods." The methylene blue employed was the double zinc salt furnished by W. Kip, 69 Barclay St., New York City. Incubations were carried on at 20° C. In some of the saltpeter experiments sterile four-ounce bottles with a tightly fitting cork stopper of good quality were utilized for the putrescibility tests. With a good grade of cork stopper there is at 20° C. incubation little danger from reaeration through leakage. As a matter of fact, glass stoppers are often interchanged and since these stoppers rarely fit perfectly in the wrong bottles, reoxygenation is more likely to occur than with the cork-stoppered bottles. The rim of the glass stoppers was covered with vaseline to prevent the absorption of oxygen as an additional precaution.

Samples which had to be stored for nitrate and nitrite examinations on the following day were preserved and put in the refrigerator, but whenever possible the determinations were made immediately.

The first question of moment was to determine whether the nitrates in a sewage, effluent, or contaminated water are drawn upon simultaneously with the free oxygen, or whether the free oxygen is eliminated alone. In a set of tabulated results, received from Mr. C. B. Hoover of Columbus in the latter part of 1912, I noted that in making incubation tests the nitrate-nitrite oxygen became in nearly all cases very low as the free oxygen disappeared and I was interested to learn whether it would work out likewise with the sewages and effluents used by me.

To make the tests, the liquid was collected in a large vessel, strained through cotton in order to get rid of the coarse suspended matter, brought up to room tempera-

Analyst, 1909, 34, p. 193.

ture gradually, and siphoned carefully, so as to avoid aeration, into glass-stoppered bottles. The crude sewage as a rule was fresh and contained considerable free oxygen in solution. On filtration through cotton the oxygen was still further increased. The dissolved oxygen, the nitrates and nitrites were determined at the start and at the time when the dissolved oxygen had just disappeared. The nitrites and nitrates were calculated as parts per million of nitrogen. The figures were carried to the first decimal place only, except where greater accuracy seemed desirable. The crude sewage used in these experiments was a fresh domestic sewage from a large sewerage area. A sprinkling filter effluent and a trade waste were used in addition.

The results obtained with crude sewage are given in Table 1.

TABLE 1.

CHANGES IN THE NITRITE AND THE NITRATE CONTENT OF CRUDE SEWAGE AT THE POINT OF FREE
OXYGEN EXHAUSTION.

Initial Dissolved Oxygen Parts per Million	Initial Nitrite as N. Parts per Million	Initial Nitrate as N. Parts per Million	Ex- haust.	Dis- solved Oxygen at End of Test Parts per Million	Nitrite at End of Test Parts per Million	at End of Test Parts per	Change in Nitrite	Change in Nitrate	crease	Nitrate De- crease Per- centage
5.0	0.08	0.7	5 6	0.0	0.1	0.5	+0.02	-0.2	25	29
5.3	0.06	0.55		trace	0.3	0.1	+0.24	-0.45	400	82
5.0	0.2	1.5	$5\frac{1}{2}$	trace	0.3	1.3	+0.1	-0.2	50	13
4.7	0.2	1.5		0.5	0.3	1.3	+o.1	-0.2	50	13
5.9	0.15	2.0	7	trace	0.3	1.4	十0.15	-0.6	100	30
5.9	0.2	1.7		0.2	0.2	1.4	0.0	-0.3	0	18
5.5	0.06	0.7	5	trace	0.2	0.6	+0.14	-o.1	233	14
4.8	0.08	0.55	41/2	trace	0.08	0.5	0.0	-0.05	ő	i
6.3	0.04	0.65	5 6	trace	0.1	0.55	+0.06	-o.1	150	9 15
5.6	0.08	0.85	6	trace	0.2	0.45	+0.12	-0.4	150	47
5.0	0.08	0.7	5	trace	0.15	0.35	+0.07	<b>⊸</b> 0.35	88	50
5.6	0.08	0.6	5	trace	0.15	0.5	+0.07	-o.1	88	17
Aver. 5.4	0.11	1.00	5 <sup>1</sup> / <sub>2</sub>	0.06	0.2	0.74	+0.09	-0.26	82	26

We observe uniformly that the nitrites are increased considerably on account of the reduction of the nitrates. Still not all of the nitrate lost at the point of free oxygen exhaustion can be accounted for in the increase of the nitrites, and there is no doubt that part of the nitrates became still further reduced, probably to ammonia and free nitrogen. The increase in nitrites of the average above (0.09 parts per million nitrogen) would only amount to 0.12 nitrate nitrogen (proportion NO<sub>2</sub> to NO<sub>3</sub>) which still leaves 0.14 p.p.m. of nitrate nitrogen or 54 per cent unaccounted for. The oxygen available from the nitrites at the start averages 0.25 p.p.m.; from the nitrates 3.43 p.p.m. or in total about 3.7 p.p.m., which is over 68 per cent of the initial free oxygen figure. The total available oxygen was therefore 9.1 p.p.m., of which there is left 0.46 p.p.m.

for the nitrites, 2.53 p.p.m. for the nitrates, which added to the very small quantity of free oxygen left amounts to a residual total available oxygen of about 3.0 p.p.m. The questions of the relation of the residual total available oxygen to the stability of a sewage after the dissolved oxygen has disappeared and whether the rate of absorption of the total available oxygen goes on in a uniform manner are discussed later.

The changes were also observed in the nitrites and nitrates at the point of oxygen exhaustion in sewages mixed with lake water in various proportions (Table 2). The Lake Michigan water is practically negligible as far as its nitrite-nitrate content is concerned. Only three experiments in all were made in this series. In the three mixtures employed there was enough oxygen present to prevent its entire complete loss and the samples were examined for nitrites and nitrates when the low point was reached.

TABLE 2.\*

Changes in the Nitrite and Nitrate Content of Crude Sewage-Lake Water Mixtures at the Point of Free Oxygen Exhaustion.

Mixture	Initial Dis- solved Oxygen p.p.m.	Initial Nitrite as N. p.p.m.	Initial Nitrate as N. p.p.m.	Dis- solved Oxygen at End of Test p.p.m.	Nitrite at End of Test p.p.m.	Nitrate at End of Test p.p.m.	Change	Change in Ni- trates	Nitrite Incr. Per- centage	Nitrate Decr. Per- centage
1S+5W 1S+6W 1S+5W	9.8 9.6 9.7	0.03 0.02 0.03	0.3 0.3 0.4	0.5 1.5 0.3	0.03 0.04 0.04	0.2 0.2 0.3	0.0 +0.02 +0.01	-0.1 -0.1 -0.1	o 50 33	33 33 25
Average	9.7	0.027	0.33	0.77	0.037	0.23	+0.01	-o.1	37	30

<sup>\*</sup> S indicates sewage; W indicates lake water.

We note again in these three tests an increase in the nitrites and a decrease in the nitrates at a point when the free oxygen is very low. The following calculation is based on the average obtained:

	Beginning of Test	End of Test
Total oxygen available Oxygen available from nitrites Oxygen available from nitrates.	10.9 p.p.m. 0.06 p.p.m. 1.1 p.p.m.	1.6 p.p.m. 0.08 p.p.m. 0.8 p.p.m.

The result of a number of similar experiments made with mixtures of crude sewage and sprinkling filter effluents in various proportions are given in Table 3. "S" again indicates sewage and "F" filter effluent. It may be mentioned that the filter effluents by themselves are non-putrescible, contain considerable quantities of nitrates and

oxygen in solution, and that the sewage was added for the purpose of making the mixtures putrescible and permitting the elimination of the free oxygen.

 $TABLE \ {\it 3}.$  Changes in the Nitrite and Nitrate Content of Crude Sewage-Filter Effluent Mixtures at the Point of Free Oxygen Exhaustion.

Mixture	Initial Dis- solved Oxygen p.p.m.	Initial Nitrite as N. p.p.m.	Initial Nitrate as N. p.p.m.	Dis- solved at End of Test p.p.m.	Nitrite at End of Test p.p.m.	at End		277	Nitrite In- crease Per- centage	Nitrate De- crease Per- centage
1S+7F	7.6	0.15	2.0	0.5	0.8	0.01	+0.65	-1.gg	433	99.5
2S+7F	6.9	0.15	1.8	trace	0.3	0.04	+0.15	-1.76	100	92
1S+7F	7.7	0.2	5.0	trace	0.25	4.4	+0.05	-o.6	25	12
1S+1F	6.6	0.2	3.3	0.8	1.0	2.2	+0.8	-r.r	400	33
1S+1F	6.1	0.15	2.6	0.9	0.55	1.8	+0.4	-o.8	266	31
Aver	7.0	0.17	2.9	0.44	0.58	1.7	+0.41	-1.2	241	41

From the average the following results are calculated:

	Beginning of Test	End of Test
Total oxygen available Oxygen available from nitrites Oxygen available from nitrates	0.38 p.p.m.	7.5 p.p.m. 1.3 p.p.m. 5.8 p.p.m.

From the average of every set of the experiments it may be noted that the loss from the nitrate-oxygen exceeds the gain from the nitrite-oxygen, so that we have to register a loss in combined nitrate-nitrite oxygen at the point when the dissolved oxygen is lowest. This loss is particularly marked in the highly nitrified sewage-filter effluent mixture, representing approximately 16 per cent of the total available or 40 per cent of the initial free oxygen present. It seems reasonable to assume that the rate of absorption of the free oxygen would be influenced by a high nitrate and nitrite oxygen content.

Since there is no doubt that the mineral-bound oxygen goes to satisfy putrescible organic matter, it is evident that the oxygen in this form must be of great importance under certain conditions. In a sprinkling filter effluent a high nitrate and free oxygen content is ordinarily taken as the index of the efficiency, yet with a high oxygen content and a low nitrate content, representing winter conditions, the effluent may be non-putrescible. Under these conditions it becomes of importance to learn the relation of the nitrate oxygen to the stability of a sewage liquid. For this purpose determinations were made in various sewage mixtures of the initial available oxygen, and the time was compared which it took for the methylene blue to disappear after all of the free oxygen was exhausted. Otherwise the technic of the test remained as previously described. A number of bottles were filled with the sewage, which had been previously brought up to 20° C. at the start, besides filling the putrescibility bottles for frequent dissolved

oxygen determinations in order to be able to determine the nitrites and nitrates at the point of free oxygen exhaustion. For convenience, the results are tabulated separately for the sewages and the sewage mixtures (Tables 4 and 5). The temperature of incubation was 20° C. as before.

PROPORTION OF TIME REQUIRED FOR THE DECOLORATION OF METHYLENE BLUE BY THE FREE OXYGEN AND THE NITRITE-NITRATE OXYGEN IN CRUDE SEWAGE.

Initial Free Oxygen p.p.m.	Initial Nitrite- Nitrate Oxygen p.p.m.	Free Oxygen Lost Hrs.	Residual Oxygen p.p.m.	Residual Nitrite- Nitrate Oxygen p.p.m.	Time of Decol- oration Hrs.	Relative Stability	Nitrite- Nitrate Oxygen at Time of Decol- oration p.p.m.	Quantity of 0.05 Per Cent Methylene Blue Solution per 150 c.c. Capacity in c.c.
7.3	1.6	8	0.1	0.3	25	21		0.85
5.9	1.8	5	trace	1.2	18	16		0.85
5.2	I.7	5.15	0.0	1.3	20	17		0.85
6.1	I . 2	6	trace	0.8	26	22		0.85
3.7	1.5	4.15	0.3	I.2	14	12		0.85
6.3	2.4	7	0.4	2.I	29	24	0.2	0.70
5.5	3.5	5	trace	2.4	20	17	0.3	1.00
5.9	7.0	7	0.0	5 · 4	41	32	0.3	0.70
5.9	6.4	6.30	0.2	5 . 2	27	22	0.2	0.70
Average 5.8	3.0	6	0.1	2.2	24	20	0.25	

Table 4 brings out a number of interesting points. Foremost is the fact that if we accept the methylene blue putrescibility test in its present form as a fairly accurate measure of the stability of a sewage, the influence of the nitrate oxygen (the nitrite-nitrate oxygen in the table above is almost entirely nitrate oxygen) in retarding undesirable anaerobic conditions is of greater weight than is commonly appreciated. The sewages above have been subjected to short aeration, in order to increase the free oxygen present, but this could not have had any influence upon the nitrates since their increase or decrease is the result of bacterial activity. It would be impossible, of course, to state definitely to just what extent a certain quantity of mineral nitrogen would influence the stability since this will depend altogether on the biologic life and the degree of decomposition of a sewage. This, as well as other observations, is given with the object of showing the general broad tendency rather than a definite numerical relation. Therefore when the average result in the table above shows that 25 per cent of the initial total available oxygen (consisting of nitrate oxygen) delayed the appearance of anaerobic conditions approximately 200 per cent as measured by the time element, it does not imply by any means that such figures will always result. One cannot fail to be impressed, however, with the uniformly decided difference in the time element required for the disappearance of the free oxygen and the nitrite-nitrate oxygen which is altogether in favor of the latter.

My early results, which were of a preliminary character and are not recorded here, were still more marked, in fact so surprising that I was led to look for grave errors in the methylene blue test as applied by me. Some interesting figures relating to this subject are contained in an article written by C. B. Hoover, who compared the methylene blue test with three other stability tests applied to sprinkling filter effluents of the Columbus sewage treatment plant and found the results of the test as apt to be misleading, because an effluent may give a very satisfactory stability when in fact only about one-half as good as indicated by the test.

Comparative tests with four different brands of methylene blue convinced me soon that the discrepancy could not be attributed to the brand which I employed. It further suggested that possibly the quantity of the coloring matter might have an influence. Such an observation has been previously made by Jackson and Horton,² who employed I c.c. of a 0.05 per cent solution for each 250 c.c. bottle capacity, while the "Standard Methods" recommends a more concentrated solution, namely I c.c. of a 0.05 per cent solution for each 150 to 200 c.c. capacity. The quantity which I have applied in the preliminary tests was I c.c. per 150 c.c. capacity, but later results were obtained with considerably lower concentrations.

There is no doubt that different results are obtained with varying quantities of methylene blue. Hence lesser concentrations of the dye come closer to indicating the absence of available oxygen. The concentrations recommended by the "Standard Methods" of the American Public Health Association, therefore, seem too high. The difference is particularly marked in the purer samples, such as filter effluents and waters moderately contaminated. A large number of tests have been carried on in this connection. The matter is still being pursued in this laboratory and will be presented in due time. In crude sewages the point raised is of course of much less weight. I feel safe in stating, however, that while the time of decoloration in

<sup>&</sup>lt;sup>1</sup> Eng. News, 1912, 68, p. 452.

<sup>&</sup>lt;sup>2</sup> Jour. Ind. Eng. Chem., 1909, 6, p. 328.

Table 4 would be considerably lower if smaller quantities of blue had been used, the results would still have been such as to give the comparatively small amount of nitrate-oxygen the greater share of the time consumed in the utilization of the initial available oxygen.

Most observers who have worked on the methylene blue test have employed an incubation temperature of 38° C., which is convenient from a practical working standpoint, inasmuch as comparative results can be more quickly obtained. It is evident that since the biologic changes, assuming that they are the same at blood temperature as they are at 20° C., will take place much more rapidly at the higher temperature, differences in the decoloration on account of varying quantities of the dye are less noticeable and therefore more likely to be overlooked. Relatively, however, slight difference at the higher temperature will equal the more marked difference at the lower, thereby resulting in serious errors of interpretation. It would be advisable to investigate the influence which different quantities of methylene blue have upon the time of decoloration, when blood temperature incubation is employed. is not likely that crude sewages would show a material difference. but fairly stable filter effluents might.

A series of tests, similar to those compiled in Table 4, were made with sewage-filter effluent mixtures, which show the same relation as discussed before. The crude sewage was not aerated previously since the mixtures contain considerable free oxygen. The amount of methylene blue employed was uniformly 0.70 c.c. per 150 c.c. capacity, therefore less than recommended by the "Standard Methods."

TABLE 5.

Proportion of Time Required for the Decoloration of Methylene Blue by the Free Oxygen and the Nitrite-Nitrate Oxygen in Crude Sewage-Filter Effluent Mixtures.

Mixture	Initial Free Oxygen p.p.m.	Initial Nitrite- Nitrate Oxygen p.p.m.	Free Oxygen Lost Hrs.	Residual Oxygen p.p.m.	Residual Nitrite- Nitrate Oxygen	Time of Decolora- tion	Relative Stability	Nitrite- Nitrate Oxygen at Time of Decol- oration p.p.m.
1S+8F	7.7 8.3 6.1 7.6	13.6 6.2 9.1 8.5	24 22 10 19	0.5 0.07 0.9 0.1	8.4 5.4 7.3 6.1	7 days 7 days 48 hrs. 33 hrs.	80 80 36 27	0.5 0.2 0.3 0.2
Average	7 · 4	g. I	19	0.4	6.8	104 hrs.	62	0.3

S indicates sewage; F, filter effluent.

Here again we are struck by the large proportion of the time element taken up by the nitrate oxygen in the decoloration of the methylene blue. In 19 hours 7.4 p.p.m. of free oxygen disappeared, while 6.8 p.p.m. residual nitrite-nitrate oxygen took an additional 85 hours, judged by the putrescibility test. The nitrite oxygen in these samples is so low as to be practically negligible. It amounts to only 0.3 per cent of the initial nitrite-nitrate oxygen. However, on account of the active nitrate reduction taking place as the free oxygen disappears, there is an increase in the quantity of nitrites at the low free oxygen point.

In connection with certain dilution experiments, carried on by me under the direction of Mr. Langdon Pearse of the Sanitary District, with a slaughter-house waste, I have had an opportunity to study the relation of its nitrate content to the time required for the decoloration of the methylene blue. The quantity of blue applied was 0.85 c.c. per 150 c.c. bottle capacity. A question mark after a result indicates that the time of decoloration has been estimated. Only such results as could be estimated with a fair degree of accuracy have been taken into account. The waste is high in organic nitrogen and the nitrates present undoubtedly originate to a large extent from various processes. Unfortunately lack of time prevented me from determining more than the initial nitrites and nitrates present and I have to assume that the nitrates are virtually eliminated at the time of the disappearance of the blue color. Nevertheless, the following table contains sufficient concrete data to be of interest.

TABLE 6.

Proportion of Time Required for the Decoloration of Methylene Blue by the Free Oxygen and Nitrate Oxygen in a Slaughtering-House Waste.

Initial		Free Oxygen	Time of De-	Relative	PERCENTAGE OF TIME OCCUPIED IN THE METHYLENE BLUE TREE BY THE	
Free Oxygen p.p.m.	Nitrite- Nitrate Oxygen p.p.m.	LOST IN HRS. APPROXI- MATELY	COLORATION HRS.	Stability	Free Oxygen	Nitrite- Nitrate Oxygen
1. 2	13.6 7.3 16.7 7.7 7.9	6 6? 6? 6? 6?	14? 14? 14 15 10	12? 12? 12 13 9	43 43 43 40 60 43	57 57 57 60 40 57
Average 3.1	10.6	6?	13	I 2	45	55

The mineral nitrogen, in this case, does not seem to have the relatively great influence upon the putrescibility observed with the sewages and filter effluents. Of the average nitrite-nitrate oxygen above only o.o p.p.m. represents nitrite oxygen. While the nitrite-nitrate oxygen is more than three times larger than the free oxygen, it seems to defer the methylene blue endpoint by only approximately 100 per cent. The free oxygen is, therefore, contrary to the former observations, in this case of greater weight than the nitrite-nitrate oxygen. This being a peculiar trade waste of a highly putrescible character, it cannot be directly compared to a normal sewage or effluent in this respect. If an explanation is called for, however, it is to be searched for in the fact that the amount of nitrate is too small to exert a stabilizing influence upon the waste. The bacterial flora is different from the one in ordinary sewage and the oxygen required is far greater than the oxygen available. It is reasonable to assume that the proportional ratio of exhaustion of the two oxygen components, the free and nitrate oxygen, will vary with the quantity of nitrate present, as well as with the oxygen consuming power of a sewage. We shall later see that the addition of a larger quantity of saltpeter to sewage is without influence upon the rate of free oxygen exhaustion and that the addition of a comparatively small quantity of saltpeter is practically without influence upon the stability.

The observations recorded in the previous tables led up to the experiments on the possible improvement of sewages on the addition of nitrates. A solution was prepared of chemically pure potassium nitrate and its strength calculated so that 1 c.c. in a 100 c.c. bottle would be equivalent to 1 p.p.m. of nitrogen, which in turn is equivalent to 7.21 p.p.m. of potassium nitrate or 3.44 p.p.m. of oxygen. A strong solution, ten times more concentrated, was prepared for experiments with larger quantities of the nitrate so as not to dilute the sample unduly. Quite a number of results were lost because the blue color disappeared during the night. Such samples, on which the time of decoloration could not be estimated fairly accurately, were eliminated altogether. In quite a number of the samples, the time could be estimated sufficiently close for my purposes.

The technic of these experiments was as follows: From a large vessel containing sewage, samples were carefully siphoned off to avoid artificial aeration into bottles containing 1 c.c. of methylene blue per 150 c.c. bottle capacity and varying quantities of the potassium nitrate solution. The bottles were then stoppered, incubated at 20° C. and the time of decoloration noted. Up to 5 p.p.m. of nitrogen were added in the form of potassium nitrate. The same sewage was employed as for the previous experiments, only settled. It was of a dilute character, containing on the average about 140 p.p.m. of suspended matter and 36 p.p.m. of chlorin. The nitrates as nitrogen vary anywhere from 0.05 to 0.20 p.p.m. in the crude sewage and from 2.0 to 5.0 p.p.m. as nitrogen in the filter effluents. The nitrites are very low, approximately 0.1 p.p.m.

as nitrogen in the sewage and 0.3 p.p.m. in the filter effluents. The free oxygen in the crude sewage as a rule was around 1.0 p.p.m.

A number of comparative experiments were made with chemically pure sodium nitrate instead of potassium nitrate and with crude saltpeter, containing 96.6 per cent of pure sodium nitrate. It was readily found that the results are identical as long as the amount of nitrate oxygen remains the same. The results obtained are therefore tabulated without reference to the brand of the chemical. Table 7 shows the results obtained on settled non-aerated sewages from the sewage testing station.

 ${\bf TABLE~7.}$  Influence of Saltpeter upon the Stability of Settled Sewages.

	SALTPETER ADDED IN P.P.M. OF NITROGEN										
	0.0	0.1	0.3	0.7	1.0	2.0	3.0	4.0	5.0		
Ī	12	I 2	I 2	I 2	I 2	16	18	20			
	23	24	26	30	32	46	58	63			
	I 2	12	I 2	12	12	19	20	23			
	36	36	36	36	38	19 48	52	64			
	22	22	22	22	24	27	29	34	1		
	12	12	12	12	14	21	23	29			
	16	16	18	19	20	22	24	26			
	14	14	14	14	16	21	25	30			
Time of Decol-	26	26	26	20	27	34	49	57			
oration of Blue	2 I	22	24	25	25	29	31	36	39		
Color in Hours	14	14	14	14	14	16	19	20	21		
	12	12	I 2	I 2	14	17	21	22	23		
	14		14			16	20	2 I	23		
	14		14			20	22	27	30		
ĺ	17	17	17	17	18	20	21	25	26		
	13	13	13	13	16	18	20	21	24		
	15	15	15	17	17	19	21	24	25		
	15	15	15	16	17	18	20	23	24		
Average	17	18	18	18.5	21	24	27	31			

Table 8 shows the improvement obtained on the addition of saltpeter to settled sewage more clearly. The average figures of Table 7 serve as the basis.

TABLE 8.

Improvement in Stability on the Addition of Varying Amounts of Saltpeter to Settled Sewages.

Saltpeter Added in p.p.m. of Nitrogen	Oxygen Equivalent in p.p.m. of Oxygen	Time of De- coloration of Blue Color Hrs.	Relative Stability	Improvement Relative •Stability Percentage
0.0	0.0	17 18	15 16	6.5
0.3	2.4	18 18.5	16 16	6.5 6.5 6.5
2.0	3.4 6.9 10.3	2I 24 27	18 21 22	20.0 40.0 46.0
4.0	13.8	31	25	66.0

The addition of upward of 2.5 p.p.m. of nitrate oxygen seems to have practically no influence upon the stability, but above that

amount the improvement is gradual and marked. The cost of improving the putrescible character of a sewage such as this, represented in the table above by about 65 per cent, would be around \$5.80 per million gallons, on the basis of crude saltpeter in carload lots at two and three-fourths cents per pound. Two hundred and ten pounds of crude saltpeter would be required per million gallons.

A sufficient storage period should ordinarily be provided, but this would depend entirely upon circumstances. Where it would be merely a question of preventing the development of anaerobic conditions in the stream, into which the sewage is to be discharged some distance below, no storage period at all may be required. On the other hand, the quantity of saltpeter to be applied need not necessarily be large enough to supply all of the oxygen for complete oxidation. Only one-half may suffice. This point would likewise depend upon local conditions and could in many cases be quite readily determined. Some subsequent practical experiments, which are reported later, have shown that no odor developed in sewages treated with a sufficient quantity of saltpeter. The sewage cleared up readily, much more so than the untreated sewage, and the sediment appeared to be of a humus-like character. These observations are in accord with those made abroad.

It is of interest to compare a sewage treated with saltpeter with a biologically treated sewage. The two liquids, altho both nonputrescible, can hardly be compared from the standpoint of actual sewage treatment. In one case we have a highly oxygenated clear liquid, low in organic constituents; on the other hand we have the original sewage with the organic matter still present but nonodorous. The transparency of a treated sewage depends upon the storage period. Probably the treatment with saltpeter should be classed as an emergency measure, which would not replace thorough biologic treatment. If the sewage be settled previous to its treatment with saltpeter, a smaller quantity of saltpeter will suffice and the results will be more uniform. The purer the liquid the less saltpeter is required, as is shown by the putrescibility results in The improvement is there indicated in the stability on adding the chemical to sewage-lake water mixtures, to sewagesprinkling filter effluent mixtures, and a contaminated river water.

In a measure, the addition of saltpeter to sewages can be compared to a high supersaturation with oxygen brought about artificially. From this point of view it is of interest to compare the effect upon the stability of simple aeration, as obtained by water falling over a dam, and the addition of saltpeter (Table 13).

I have subsequently made a number of tests to show the quantity of saltpeter necessary to obtain perfect stability of our plain settled sewage and found that an addition of 12 to 18 p.p.m. of nitrogen in the form of saltpeter, representing 41 to 62 p.p.m. of oxygen would do, except when the sewage happened to be a storm water sewage. This would make the cost for chemicals of treating such a settled sewage from \$17 to \$26 per million gallons of sewage. This is based on the assumption, however, that the sewage will receive no other oxygen than the saltpeter oxygen for 20 days, this representing the length of exposure in the methylene blue bottle. It is plain that this standard is very severe and that in most cases it would probably be ample to accept a four days' decoloration as sufficient, in which case, of course, the cost of the saltpeter would be considerably less.

Approximately 50 per cent of the suspended matter in the sewages employed could be settled. For crude, unsettled sewages more saltpeter would be required to obtain like results. A fairly large number of tests would seem to indicate that for the same dry weather sewage, unsettled, approximately 24 to 30 p.p.m. of nitrogen in the form of saltpeter, representing 82 to 103 p.p.m. of oxygen, is necessary, which would make the cost of the chemical between \$35 to \$43 per million gallons. This again is on the 20 days' stability basis.

This investigation was not originally undertaken to determine the merits of the saltpeter treatment of sewage or to suggest such a method as a substitute for the present methods in vogue. The figures on the cost of chemical are given merely because this phase of the problem has presented itself incidentally to the purely technical investigation of the influence of nitrates upon the stability. It is of interest to compare the approximate costs of chemical for this treatment in the United States and abroad. In the United States, the sewages are by far more dilute than on the continent. Weldert has stated that approximately 8,300 pounds of Chile saltpeter are required for the treatment of one million gallons of sewage. This would make the cost of the chemical alone about \$230, based on a cost of two and three-fourths cents per pound. It would probably require about 800 pounds at a cost of about \$22 to treat a million gallons of our weak nonsettled sewage. The difference in the cost of the treatment of the continental and our sewage can probably be explained by the difference in the dilution of the two. Many factors are involved in this process, all tending to make any figure subject to great variations. My figures are based purely on the particular sewage employed in these experiments. I cannot emphasize strongly enough that each case represents a different problem. This may alter any of the figures cited above materially one way or the other.

A number of results on the addition of saltpeter to sewage-lake water mixtures have been obtained and are given in Table 9.

	TABLE	Ε 9.	
INFLUENCE OF SALTPETER	UPON THE STABILITY	OF CRUDE SEWAGE-LAKE	WATER MIXTURES.

		PROPORTION OF SEWAGE								
	0.0	0.1	0.3	0.7	I.O	2.0	3.0	4.0	5.0	TO WATER
	34 72	34 72	34 76	40 90	44 96	49 216	72 480*			1S+5W 1S+6W
Time of Decoloration of Methylene Blue	60 65	60 67	65 120	77 192	132 480*	480*				1S+6W 1S+5W
Color in Hrs.	19 20	20	2I 24	21	22	26 25	29 26	31 26	35 27	1S+1W 1S+1W
	25 23		30 23			41 27	50 32	60 34	84 38	3S+4W 2S+1W

S indicates sewage; W stands for water.

It is not fair in this case to strike an average since a number of results are missing, and since the samples, which held out longer than 20 days cannot be properly counted in. It is plain that the more dilute mixtures require considerably less saltpeter to make them stable than do the more concentrated mixtures. This, of course, is due to the fact that the dilute mixtures contain less organic matter and more free oxygen in solution.

Since most of the sprinkling filter effluents at my disposal were nonputrescible, I had to add various amounts of sewage in order to be able to observe the effect of the addition of saltpeter upon the stability. In Table 10 are shown the results obtained, F indicating filter effluent.

<sup>(\*)</sup> indicates that the blue color persisted after 20 days.

				TABLE	10.			
INFLUENCE OF	SALTPETER	UPON	THE	STABILITY	OF	SEWAGE-FILTER	EFFLUENT	MIXTURES.

		PROPORTION OF SEWAGE								
	0.0	0.1	0.3	0.7	1.0	2.0	3.0	4.0	5.0	TO FILTER EFFLUENT
Time of Decoloration of Methylene Blue Color in Hrs.	24 89 192 46 28 180 86	24 108 192 49 30 180	24 120 252 52 32 192 96	24 144 324 58 44 240 108	27 168 372 61 49 264 120	30 288 396 68 58 480* 156	30 384 480* 132 62	39 480*  180 68	252	7S+4F 1S+1F 1S+8F 1S+8F 2S+7F 1S+7F 1S+2F

<sup>(\*)</sup> again indicates the persistence of the blue color at the end of 20 days.

Table 11 shows the results obtained with the addition of saltpeter to liquid taken from the main channel of the Sanitary District. The average analysis at the time when the tests were made was approximately as follows:

Total suspended matter	53	p.p.m.
Volatile suspended matter	15	p.p.m.
Fixed suspended matter	38	p.p.m.
Oxygen consumed	15	p.p.m.
Free ammonia as nitrogen	1.0	p.p.m.
Organic nitrogen as nitrogen	1.6	p.p.m.
Nitrites as nitrogen	0.04	p.p.m.
Nitrates as nitrogen	0.5	p.p.m.
Chlorin		p.p.m.
Alkalinity (as Ca Co <sub>3</sub> )	32	p.p.m.

TABLE 11.

Influence of Saltpeter upon the Stability of a Contaminated Water.

		SALT	PETER A	DDED IN I	P.P.M. OF	Nitrogei	٧.		DISSOLVED
	0.0	0.1	0.3	0.7	1.0	2.0	3.0	4.0	OXYGEN ON SPOT
Time of De- coloration of Methylene Blue in Days	8 53 hrs. 8 82 hrs. 84 " 48 " 44 " 33 "	8½ 8 4½ 5 72 hrs. 46 " 70 "	10 86 hrs. 11 7 51  50 hrs. 78 "	11½  17½ 8 8 7½ 54 hrs.	20* 4½ 20* 9 9½ 10 73 hrs.	12½ 20* 20* 20* 20* 20* 20*	10	20*	8.5 4.3 5.3 2.1 3.8 1.8 2.0

<sup>(\*)</sup> indicates that the color persisted after 20 days.

The addition of about 1 p.p.m. of nitrogen in the form of saltpeter makes the unstable canal water sufficiently stable for all practical purposes, but the procedure would be too costly. If a nuisance is to be attacked by this method of treatment at all it can only be attacked by treating the sewage proper, before it has a chance to deoxygenate the river water to the point of the development of odors.

The question is important as to whether the addition of saltpeter has any influence upon the exhaustion of the free oxygen in solution and upon the period of what Phelps styles "oxygen avidity." It is during the period of "oxygen avidity" when the oxygen is on the negative side of the exhaustion curve that nuisance is likely to set in. For this purpose a number of different sewages have been collected in large battery jars and saltpeter added in quantities equivalent to 5 p.p.m. of nitrogen, representing 17.2 p.p.m. of oxygen or 30.3 p.p.m. of sodium nitrate. A "blank" experiment on the same sewage free from saltpeter was carried on at the same time for the sake of comparison. The nitrites and nitrates are expressed in parts per million of nitrogen. The results of the tests are given in Table 12.

The nitrites invariably increased in the sewage treated with saltpeter and in this respect my observation coincides with those of Bach and Guth and Keim. Glaser, as previously mentioned, denies that nitrites are formed during the reduction process.

The effect on purer liquids, such as badly contaminated river waters, of incubation with saltpeter in open vessels has not been studied. The question is therefore open whether saltpeter has a retarding effect upon the deoxygenation of waters which normally do not lose their entire free oxygen on storage. The indications are that sewages lose their free oxygen, whether a reasonable quantity of saltpeter is added or not. It did not seem necessary to use greater quantities of saltpeter than were employed. A distinct difference was noticeable in the appearance of the sewage treated with saltpeter and the "blank" sewage. The "saltpeter" sewage did not develop a putrid odor and also clarified itself long before untreated sewage did. Incidentally, it may be mentioned—and this perhaps is an important point—that when a sewage treated with saltpeter is discharged into a watercourse, the presence of mineral nitrates will greatly promote the development of plankton, which, stimulated by sunlight, furnishes an abundance of free oxygen immediately available for the oxidation of organic sewagic matter.

The striking feature of Table 12 is the comparative rate of reoxygenation of the treated sewage and untreated sewage. The period of "oxygen avidity" is considerably shortened. It does not matter whether the free oxygen is exhausted as quickly in the

nitrated sewage, inasmuch as the sewage is in fact provided with sufficient available oxygen to prevent putrefaction. The addition of 5 p.p.m. of nitrogen in the form of saltpeter is equivalent to the

TABLE 12. Influence of Saltpeter upon the Oxygen Exhaustion and Reoxygenation of Sewages and Sewage Mixtures.

	Sal	tpeter Sev	AGE	"Blank" Sewage			
MIXTURE	Time Elapsed Hrs.	Dissolved Oxygen p.p.m.	Oxygen Increase p.p.m.	Dissolved Oxygen p.p.m.	Nitrite	Nitrate	
Crude sewage	Start  4 8 10 14 18 25 42 66	3·3 2·3 0.08 0.0 0.0 0.4 0.6 3·4 6.2	0.4 0.6 1.1 2.0	3·3 2·3 0·08 	0.2	0.35	
3 Pts. crude + 1 Pt. septic + 1 Pt. settled sewage	Start  4 6 25 66	2.6 1.8 0.0 0.4 2.0	0.4 1.9	2.5 1.8 0.0 0.0	0.3	0.1	
Septic tank effluent	Start 4 25 66	0.5 0.0 2.7 9.8	o.6 3.0	0.5 0.0 2.1 6.8	0.2	O. I	
Settling tank effluent	Start 6 10 42 66	1.7 0.3 Trace 6.3 10.4	I.5 2.2	1.6 0.3 Trace 4.8 8.2	0.3	0.6	
Crude sewage	Start 29 70 94	5·3 Trace 2.1 3.0	2.I 3.0	5·3 o.o o.o Trace			

Incubation in Closed Bottles with 4 p.p.m. of Nitrogen as Saltpeter.

5 Pts. sewage + 1 Pt. lake water	Start 19	8.o o.3	 8.0	
r Pt. sewage + 7 Pts. filter	Start 2½ 21	8.3 7.1 0.14	 8.3 7.1 0.07	
Crude sewage	Start 4 5	5.5 o.6 Trace	 5.5 0.3 Trace	

addition of 17.2 p.p.m. of oxygen in a convenient form. If a sewage be aerated at a temperature of 20° C., at best only about 9 p.p.m. of dissolved oxygen is added. This ordinarily is not sufficient to permit aerobic destruction of the putrescible matter present.

Besides aeration other means are not readily available to supply a sufficient amount of oxygen, unless by dilution with fresh water or by the addition of saltpeter.

In order to avoid a serious misunderstanding when comparing these two means of supplying sufficient oxygen, it is very important to remember that an ample dilution with fresh water, if such can be had, is by far the more preferable procedure, disregarding altogether the question of cost. Free oxygen is immediately available for the oxidation of malodorous decomposition products and stimulation of aerobic bacteria. Odors disappear quickly, not because the intensity is lessened in proportion to the dilution, but because the compounds responsible for the odor are actually oxidized. Moreover, the diluted sewage is a physical improvement over raw sewage. The esthetic feature is of importance, althosubordinate to the question of actual nuisance. In the dilution method we have therefore an immediate means of relief. not so with the saltpeter method. This method is a prophylactic measure rather than a curative, if I may express it that way. Where an actual nuisance exists, saltpeter will not relieve it at once. There is no immediate chemical reaction between the saltpeter oxygen and the malodorous decomposition products. The saltpeter oxygen becomes available through bacterial activity and its presence will undoubtedly shorten the period of actual nuisance. This will depend, however, upon the progress of decomposition and the amount of nitrite-nitrate oxygen present at the time when the free oxygen has disappeared. The case is different where the prevention of a nuisance is aimed at. A sewage sufficiently dilute in character, or a strong sewage sufficiently diluted with fresh water, may run in an open channel for a considerable period before a live nuisance will develop. Saltpeter added to such a sewage at the point of origin may prevent a nuisance farther down. The time required and the quantity of saltpeter necessary are capable of close determination in the laboratory.

From the standpoint of fish life, a study of Table 12 shows that the addition of saltpeter would not be of immediate benefit, since the essential free oxygen disappears regardless of the saltpeter. The benefit would be derived from the improved ratio of reoxygenation and the increase in plankton, which serves as fish food.

Tests were made to reach a conclusion on the comparative value from the putrescibility standpoint of simple aeration, like that caused by water running over a dam, and the artificial addition of saltpeter. Sewage was aerated and methylene blue tests made on the liquid before and after aeration. To a series of putrescibility bottles containing the nonaerated sewage, various quantities of saltpeter, representing small amounts of available oxygen, were added and the time of decoloration compared with the time required by the aerated sample. The improvement in the aerated sample must necessarily be ascribed to the increased free oxygen. The dissolved oxygen was determined before and after aeration. The results obtained are given in Table 13.

TABLE  $1_3$ .

Improvement in the Stability of Crude Sewages on Aeration and on the Addition of Saltpeter.

		SALTPE	rer Adi	DED IN	Initial Free Oxygen	INCREASE OF FREE OXYGEN AFTER	Stability after Aeration			
	0.0	0.34	1.02	2.38	3 · 44	6.88	10.32	IN P.P.M. AERATION P.P.M.	Hrs.	
	17	i <sub>7</sub>	17	17	18	20	21	4.3	3.9	18
Time of De-	15	15	15	17	17	19	21	3 · 5	3.2	17
coloration	15	15	15	16	16.5	18.5	20	3 · 4	4.5	17.5
Hrs.	15	15	15	16	16	17	18	3.2	4.I	17
1113.	16	16	10.5	16.5	16.5	16.5	18	2.8	5 · 4	17
	I 2	13	14	14	14	16	17	3.0	5.2	16
Average	15	15	15.4	16	16.3	17.8	19.2	3 · 4	4.4	17.1

We note in the average of above table an increase of 4.4 p.p.m. of oxygen on aeration, which retards the disappearance of the blue color in the putrescibility test by approximately two hours. To bring about such an improvement requires the addition of saltpeter equivalent to 5 p.p.m. of oxygen or 8.8 p.p.m. of saltpeter. Considering the difficulty of obtaining accurate readings of the methylene blue endpoint, there is a fairly close agreement between the improvement in the stability on aeration and the addition of saltpeter.

The question of making sludges nonputrescible by the addition of saltpeter has not been studied, partly because it appears practically a hopeless task from a financial point of view, and partly because there appears to be no advantage to be gained in such treatment. The drying of the sludge in sewage treatment plants in the United States is accomplished without nuisance. As a general proposition, it is much cheaper to have the air and the sunlight mineralize the sludge, even tho it takes longer.

The writer is now studying the possibility of utilizing the addi-

tion of nitrate in laboratory tests to indicate the quantity of oxygen required by sewages, effluents, or streams for complete oxidation. Such information is now obtained by various methods involving dilutions with fresh water. Either the rate of exhaustion of the free oxygen is observed or the dilution is found which is necessary to prevent the decoloration of the methylene blue. Anyone who has tried such dilution tests realizes that the procedure of making dilutions with fresh water is tedious, requiring very great care to avoid aeration. These difficulties become still more pronounced when such tests are attempted in the field. If correct results can be obtained by merely adding to putrescibility bottles different amounts of saltpeter, representing definite equivalents of oxygen, then incubating the bottles at 38° or 22° C., according to time in which the information is desired, the field tests would be very simple. In order to obtain approximate information on the quantity of oxygen needed to complete the oxidation, a blank putrescibility test could be added, and by comparison with the other putrescibility bottles, the information would be gained by noting the smallest quantity of "nitrate" oxygen which will prevent decoloration. If the total quantity of oxygen required is desired, the initial free oxygen, the nitrites, and the nitrates, should be also determined. With incubation at 37° C., results sufficiently close for all practical purposes could be obtained in four days. As a rule, such information is not wanted so urgently that a few days' delay would constitute a serious drawback. The writer is working on such tests and hopes to have material to present later.

The experiments described deal with the direct influence of the nitrates upon the stability. However, since nitrites are formed during the process of nitrate digestion it may be of interest to comment briefly on the relation of nitrite oxygen to the stability.

Nitrites were added artificially in the form of chemically pure sodium nitrite to samples of sewages, sewage-filter effluent mixtures, and polluted water in quantities of 0.2,0.5,1.0,3.0, and 5.0 p.p.m. of nitrogen. The oxygen equivalents of these quantities vary from 0.45 to 11.5 p.p.m. Less oxygen is of course available from the nitrite than from a corresponding amount of nitrate. The oxygen must ultimately be utilized for the oxidation of organic matter. In

most cases, and in particular with the purer samples, the addition of nitrites resulted in a corresponding improvement of the putrescibility as indicated by the methylene blue test. In a number of crude sewages, however, the addition of even 5 p.p.m. of nitrogen as nitrite showed but little if any improvement in the stability. striking feature observed when nitrites are added to the putrescibility bottles containing crude sewages is the tendency to the reabsorption of atmospheric oxygen. The catalytic action of the nitrites or of the products resulting from their decomposition is pronounced. Manipulation must be very carefully conducted, or the results obtained may be entirely misleading on account of the great affinity of such a liquid for atmospheric oxygen. Frequently a nearly decolorized putrescibility bottle containing sewage has been found to reabsorb oxygen and turn blue inside of a few hours, when the stopper was intentionally slightly loosened, while putrescibility bottles containing decolorized sewage may be loosely stoppered or even contain an air bubble without absorbing the oxygen throughout. Unless the bottle is shaken the reaeration will show only on the surface. The necessity is therefore apparent for employing seals for putrescibility bottles, even when an incubation temperature of 20° C. is used, when effluents are studied which are high nitrites or which form high nitrites on decomposition. Hoover' comments on the fact that the methylene blue test is misleading in that the consumption of oxygen in a mixture of water and sprinkling filter effluent is more rapid than in the undiluted sample. His observations are based on incubation at blood temperature, which may not be strictly comparable to observations at 20° C. To a certain extent, it is likely that the phenomenon was due to the oxygen-retaining property of the nitrites, a property which correspondingly weakened in the diluted sample. The fact that the nitrites are the last oxygen-carrying compounds to disappear before anaerobic conditions set in, is in this respect significant. While we know but little of the mechanism of the nitrate reduction as taking place in the decomposition of sewages we have yet to learn a great deal about the rôle which the nitrites play in this process. The physical chemist is the one likely to find an answer to the question.

Loc. cit.

## SUMMARY.

- 1. At times there may be enough nitrate-oxygen and nitrite-oxygen present in sewages to prevent ultra-anaerobic conditions. There is a tendency to overlook this point. The influence of oxygen from that source is of greater weight in preventing a nuisance than is commonly appreciated.
- 2. On incubating sewage mixtures under exclusion of air up to the point of free oxygen exhaustion the nitrites are increased, the nitrates decreased. The loss from the nitrate-oxygen exceeds the gain from the nitrite-oxygen.
- 3. The concentrations of the methylene blue solution as recommended in the "Standard Methods of Water Analysis" by the American Public Health Association seem too high. This is being investigated further in this laboratory and will be presented at the 1913 annual meeting of the American Public Health Association.
- 4. Experiments on the addition of saltpeter to the weak domestic sewage of the 39th Street sewerage area in Chicago have demonstrated that it requires approximately 24 to 30 p.p.m. of nitrogen in the form of saltpeter, representing 82 to 103 p.p.m. of oxygen, to obtain complete stability. The cost of the chemical would vary between \$35 to \$43 per million gallons. Settled sewage would require 12 to 18 p.p.m. of nitrogen in the form of saltpeter, representing 41 to 62 p.p.m. of oxygen. This would make the cost of treating the settled sewage from \$17 to \$26 per million gallons.
- 5. The cost of treating a weak American sewage with saltpeter is much less than the cost of treating a German sewage, probably on account of the higher dilution.
- 6. The addition of a moderate quantity of saltpeter (equivalent 5 p.p.m. of nitrogen) is without influence upon the rate of free oxygen exhaustion but shortens the period of oxygen "avidity." The addition of a comparatively small quantity of saltpeter (under the equivalent 1 p.p.m. of nitrogen) seems to be practically without influence upon the stability of sewages. The nitrites are invariably increased by the addition of saltpeter to sewage.
- 7. The addition of 1.0 p.p.m. of nitrogen in the form of saltpeter makes the putrescible waters of the drainage canal of Chicago

stable for all practical purposes, but the procedure is too costly to be of more than theoretical interest.

- 8. Sewage treated with sufficient saltpeter does not develop a putrid odor and clarifies itself long before an untreated sewage will.
- 9. The dilution of sewage with fresh water is greatly preferable to the addition of saltpeter, disregarding altogether the question of cost. The dilution method furnishes an immediate means of relief which is not the case with the saltpeter method, in which the sewage may have to be stored for varying periods in order to obtain a fair degree of stability. To fish life the saltpeter treatment is of no immediate benefit for the reason that the essential free oxygen disappears regardless of the presence of the chemical.
- 10. Experiments have demonstrated that the oxygen obtained by aeration exerts the same effect upon the stability of sewages or contaminated waters as an equivalent quantity of saltpeter-oxygen.
- 11. The addition of saltpeter may be utilized in connection with the methylene blue putrescibility test to obtain information on the amount of oxygen necessary to complete the oxidation of a sewage or effluent. This method is now being tested in the laboratory of the Sanitary District of Chicago.
- 12. The addition of nitrites also improves the stability of sewage mixtures. Such a treated sewage has a strong tendency to absorb atmospheric oxygen.

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